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ADDITION OF REFRACTORY COMPOUNDS TO MOLTEN ZIRCONIUM

by

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Nuclear and Powder Metallurgy Section

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INTRODUCTION

Dispersion strengthening has received much attention in recent years as a means of improving the elevated-temperature strength of metals and alloys. In the course of studies on dispersion strengthening of zirconium, being carried out in these laboratories, the effect of direct addition of refractory compounds to zirconium during arc-melting has been investigated. This note deals with effects obtained by making additions of ThO_2 to zirconium in this manner.

EXPERIMENTAL PROCEDURE

The alloys studied in this investigation are listed in Table 1. These alloys were prepared in a laboratory-size tungsten-arc furnace. Melting

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and alloying were carried out in a water-cooled copper hearth in an argon atmosphere.

Reactor-grade zirconium sponge containing 1100 ppm oxygen was consolidated by melting it into a dense button in which a cavity was drilled to contain ThO_2 powder. Each charge weighed approximately 75 grams and was remelted at least 4 times to ensure homogeneity. The final melt was made in a hearth that produced a "cigar-shaped" ingot.

The Zr-0.64% Th, Zr-0.34% ZrO_2 and Zr-0.64% Th-0.34% ZrO_2 alloys were prepared to determine the effect of thorium and oxygen separately and together, arising from any possible decomposition of the ThO_2 . The 0.64% Th and the oxygen in 0.34% ZrO_2 are equivalent to the thorium and oxygen in 0.7% ThO_2 .

Some arc-melted ingots were swaged in air at 500°C to 0.35-in.-diameter rods. All heat treatments were carried out in vacuum.

The tensile test specimens, of 1-in. gauge length and 0.16-in. gauge diameter, were tested at 650°C in vacuum after being held at temperature for 1 hr.

Specimens for microexamination were chemically polished in a solution containing 45 cc distilled water, 45 cc nitric acid and 8 to 10 cc hydrofluoric acid.

RESULTS

Microexamination of Zr-0.7% ThO₂ and Zr-0.64% Th alloys, swaged and heat-treated, revealed that particles of a second phase were present in Zr-0.7% ThO₂ but absent from Zr-0.64% Th. A similar phase in the Zr-2% ThO₂ alloy was identified as ThO₂ by X-ray diffraction analysis after specimens were heat-treated at 800°C for 24 hr to coalesce the particles.

In Zr-2.5% ThO₂ arc-melted specimens, the ThO₂ particles were located at alpha-platelet boundaries and, as indicated above, their size could be altered by heat treatment. Heat treating at 950°C for 6 hr followed by water quenching reduced the size of the alpha-platelets and the ThO₂ particles, some of the latter being 0.03 micron in size. Heat treatment at 1400°C for 24 hr followed by furnace cooling, enlarged the alpha-platelets and also the ThO₂ particles, which were about 3 microns in size.

When specimens of the Zr-2.5% ThO₂ alloy were water-quenched from the molten state (levitation-melted in argon), second-phase particles were not evident in the microstructure. However, on ageing these specimens at 700°C for 6 hr, second-phase particles could be readily seen.

Table 1 lists the results of tensile tests carried out at 650°C on the Zr-ThO₂ alloys in various metallurgical conditions. All the alloys containing 2.5%, or more, ThO₂ had high-temperature tensile strengths

greater than that of Zircaloy-2. Specimens of the Zr-0.7% ThO₂ alloy that were swaged at 500°C and heat-treated at 700°C for 6 hr had an ultimate tensile strength of 23.6 kpsi compared with 16.2 kpsi for as-arc-melted specimens.

It can be seen that the tensile strengths of Zr-0.64% Th, Zr-0.34% ZrO₂ and Zr-0.64% Th-0.34% ZrO₂ were less than half that of Zr-0.7% ThO₂ specimens swaged and heat-treated, and substantially below that of Zr-0.7% ThO₂ as-arc-melted. It is interesting to note that addition of thorium and oxygen to zirconium did not produce the same effect as addition of ThO₂. Possible chemical reactions between zirconium and refractory compounds at elevated temperatures are being investigated.

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TABLE 1

Tensile Properties of Zirconium and Zirconium Alloys at 650°C

Nominal Composition	Condition	UTS, kpsi	0.2% YS, kpsi	% El., on 1 in.
Zr	As-Arc-Melted	11.2	7.5	44
Zircaloy-2	As-Arc-Melted	17.6	11.9	42
Zr-0.64% Th	Swaged 500°C, HT 700°C 6 hr, WQ	9.5	4.7	63
Zr-0.34% ZrO ₂	Swaged 500°C, HT 700°C 6 hr, WQ	10.0	5.6	59
Zr-0.64% Th- 0.34% ZrO ₂	Swaged 500 C, HT 700°C 6 hr, WQ	9.7	4.0	66
Zr-0.7% ThO ₂	Swaged 500 C, HT 700°C 6 hr, WQ	23.6	14.7	48
Zr-0.7% ThO ₂	As-Arc-Melted	16.2	10.9	36
Zr-2.5% ThO ₂	As-Arc-Melted	23.7	16.8	27
Zr-3.5% ThO ₂	As-Arc-Melted	27.0	17.3	35
Zr-5.0% ThO ₂	As-Arc-Melted	26.6	17.7	26
Zr-7.0% ThO ₂	As-Arc-Melted	25.5	16.3	20
Zr-2.5% ThO ₂	HT 650°C 6 hr, WQ	26.1	17.5	22
Zr-2.5% ThO ₂	HT 950°C 6 hr, WQ	23.7	16.5	27